Author response to the review of Oyabu et al. "Fractionation of O_2/N_2 and Ar/N_2 in the Antarctic ice sheet during bubble formation and bubble-clathrate hydrate transition from precise gas measurements of the Dome Fuji ice core"

We would like to thank Dr. Nanna B. Karlsson for handling our manuscript and the two anonymous reviewers for their valuable comments. Our responses are explained below. Our replies are in blue and reviewer comments are written in *black italic letters*.

Reply to the Editor (14 September 2021)

We corrected the typo in the new figure ("remaininig" -> "remaining").

Reply to Referee #1 (05 July 2021)

This paper reviews all of the non climatic mechanisms responsible for dO2/N2 fractionation in ice cores, and includes a compilation of most existing measurements, in addition to a large dataset of new measurement from the Dome F ice core, with a variety of sampling strategies.

It is an extremely useful and valuable paper, that clearly identifies optimal strategies for sampling ice cores to retrieve a valuable dO2/N2 signal. In particular, the authors did a great effort in cutting the ice in various ways to identify where and how dO2/N2 fractionation was happening, both between outer and inner ice samples, and with high resolution vertical sampling. Their new datasets shed new light on processes affecting gas loss in ice cores. The paper is very well written, the scientific quality of the analyses is excellent, and the figures are also very clear. Although I have a few important comments on the presentation of the results, I recommend its rapid publication.

Major comments:

1. Section 4, called "Discussion" actually has results in it, and I am missing a "discussion" section that would include perspectives. I think it would be valuable to add a small "perspective" section, devoted to next steps: Do you think that everything is known about the different mechanisms of fractionation? What could/should be done next to improve either our understanding and isolation of the various processes, or improve the corrections? In particular, a summary on how your data could be picked up by ice physicists to test hypotheses about the mechanisms that you talk about in the paper would be an important addition, to make sure that your results are re-used.

We moved the results of the diffusion model (L368 – 376 in the original text) to section 3.4 in the Results chapter.

For the perspective, we added the two paragraphs in the Conclusion chapter and deleted the last part of the first paragraph of Conclusion of the original text.

2. Related to my first comment, I am missing a summary at the end of the paper of the optimal sampling strategy. I think it would be great, either to add it to the conclusion, or to have a "sampling strategy" summary section, separated for each of the zones that you added. This section could summarize for each zone, the mechanisms controlling non gravitational d02/N2 signal, and how to mitigate these.

The magnitude of the post-coring gas loss depends on the ice-core quality, sample size and dimensions, and storage temperature and period. The frequency and magnitude of the natural fractionation in the BCTZ might be related to the annual layer thickness and impurity concentrations. Therefore, an optimal sampling strategy for the Dome Fuji ice core should not be readily applicable to other ice cores. Instead, we added our recommendations for finding the optimal sampling strategy for other cores in section 4.5.

3. For someone who is not close to the literature of O2/N2, it would be good to have, maybe in the introduction, or in your discussion section, a schematics of the fractionation mechanisms. You may have to have 3 or 4 of them, for each of your zones, and maybe one more for post-coring. Generally speaking, all of the mechanisms are discussed in a hand-wavy matter, and it's a bit difficult, through the reading of your paper, to understand what hypotheses about what mechanisms are actually testable or tested in your presentation.

We added a schematic in the revised manuscript (Figure 11).

4. In the conclusion, in addition to specific recommendations for sample handling and storage to avoid fractionation in the first place, I am missing an optimal strategy for correcting for gas loss. You find different slopes of O2/N2 vs Ar/N2 and for d180 vs O2/N2. I wonder if you could separate out the different mechanisms involved in "gas loss" fractionation, and provide several sequential correction strategies that could account for these differences, valid across different zones and different cores, to make it less heuristic.

We did not propose a universal method of correction for all ice cores, because there are many determining factors on the post-coring gas loss (e.g., drilling quality, storage condition just after coring, and size, dimensions, temperature and period during the storage, etc.), which cannot be separately and quantitatively evaluated. Thus, we think it is sufficient to propose the method for excluding the gas-loss fractionation from the ice-core dataset, as we describe in the original manuscript.

For reference, empirical correction methods for $\delta O_2/N_2$ and $\delta^{18}O$ have been successfully established from fractionated datasets (e.g., if there is a clear relationship between $\delta O_2/N_2$ and the storage period, or between$\delta^{18}O$ and $\delta O_2/N_2$) (Kawamura et al., 2007; Severinghaus et al., 2009).

Detailed comments:

1. You don't explain clearly what you mean in the figures by dO2/N2_grav. It's only explained in Figure 8, but you use it already in Fig 4. You should briefly explain in Section 2 how (and why) you correct for gravitational fractionation, and introduce your notation.

We added the explanations and equations in the third paragraph of section 2.2.

2. The section on your diffusion model is a bit difficult to understand. In the main text, you should start by saying what you want to do with this model, what you want to test. Do you want to validate the effective diffusivity? Do you want to predict how much diffusion there will be in newly drilled deep ice cores, to inform the sampling strategy?

Then you might consider including the main equation, it does not take too much space, but helps the reader. It's maybe more useful than the Argon diffusivity (which is also described in the appendix), since O2 is the focus of your paper.

Finally, you need to describe better what you use for inputs, what you use for outputs, what are the tunable versus known parameters. In the main text, you need to have a sentence or 2 that have enough details that the reader understands what you are trying to do, and in the appendix, you need to add more details. As it is now, there is not enough information to reproduce your results. Can you describe more the model set up? How deep, the discretisation scheme you used, how long you ran it for, the input that you used, the outputs that came out.

We aimed at testing with the model whether the observed homogeneity of the gas composition below BCTZ is quantitatively consistent with molecular diffusion in the ice sheet, with the independently proposed permeabilities of N_2, O_2 and Ar by previous authors. The prediction of gas diffusion for future ice corings is beyond the scope of this study, because it requires more advanced model setups (for significantly thinned ice near bedrock) and evaluation of temperature dependence of diffusivity.

We added the main equation and a few associated equations that would help the readers (section 2.4).

- $\frac{\partial C_m^h}{\partial t} = \frac{\partial}{\partial z}\left(D_m \frac{\partial C_m^h}{\partial z}\right)$ (diffusion equation)
- $C_m^h = S_m P_m^d X_m$ (concentration of m-molecule (m = N_2, O_2 or Ar) dissolved in ice in equilibrium with clathrate hydrate)
- $log P_m^d = a_m - \frac{b_m}{T}$ (dissociation pressure)

According to the comment, we modified section 2.4 and Appendix A.

3. Regarding the input of the diffusion model, have you considered using a tuned version of the Ca record, since the O2/N2 seems well correlated with Ca, rather than reproducing a shallow segment of data? There is a funny offset in your figures, that I presume cannot be interpreted, but it would be interesting to see if we could use Ca2+ your diffusion model as a predictor (and then, maybe, as a correction factor).

Following the suggestion, we conducted simulations with the scaled Ca^{2+} data as the model's initial states. As we have two depths with detailed chemistry data along with the gas data (1258 m and 1399 m), we used the 1258 m data to establish the Ca-$\delta O_2/N_2$ and Ca-$\delta Ar/N_2$ relationship. We converted the 1399-m Ca record to $\delta O_2/N_2$ and $\delta Ar/N_2$, and used them as the initial state at 1258 m (we also considered the ice thinning). The model results with the permeability of Salm01 and Ar(II) are shown below. For both $\delta O_2/N_2$ and $\delta Ar/N_2$, the model results agree with the data rather well in terms of the number of wiggles and their positions, as the reviewer speculated. However, the amplitudes are both overestimated and underestimated by the model (e.g., the model overestimates the amplitude at 1399.1 m and underestimates at 1399.25 m for both $\delta O_2/N_2$ and $\delta Ar/N_2$). As the initial states of $\delta O_2/N_2$ and $\delta Ar/N_2$ would not be perfectly reconstructed by scaling the Ca record, some mismatches would be expected (some other impurities such as Na and Mg might also be related because they are also highly correlated with $\delta O_2/N_2$).

This modeling exercise has the advantage that it doesn't have the arbitrariness of the relative phases in comparing the model results and data. However, the application of this alternative input is limited to only one case (1399 m) with a few wiggles. Thus, we would rather refrain from adding it to the manuscript.

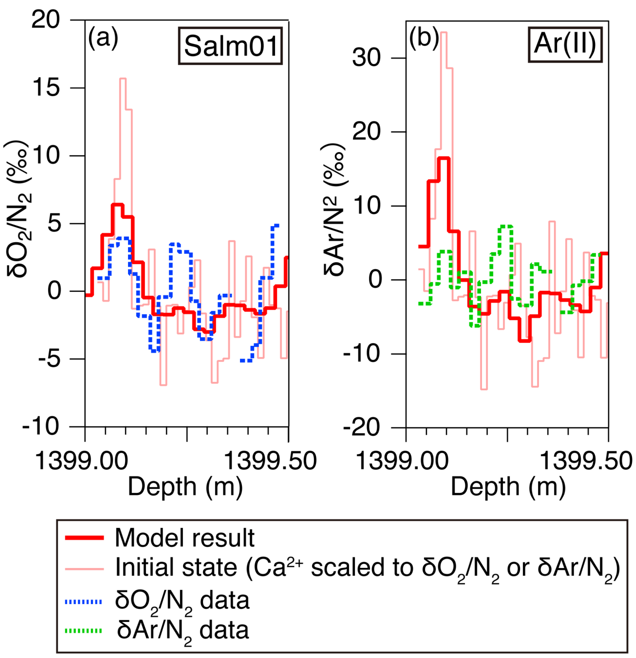

Figure caption: Comparison of the diffusion model outputs for (a) $\delta O_2/N_2$ and (b) $\delta Ar/N_2$ with Salm01 and Ar(II) permeation parameters (red lines) and high-resolution data (blue and green dotted lines) at 1399 m. For this simulation, the initial states were constructed from the measured [Ca^{2+}] profile with linear equations established from the data at 1258 m; $\delta O_2/N_2 = 2.8033\ [Ca^{2+}] - 33.55$ and $\delta Ar/N_2 = 5.9868\ [Ca^{2+}] - 61.467$.

4. Raman spectroscopy is not described at all (line 186). You could add a sentence or 2 describing how this technique does, what it shows. I expect your readership will have a lot of ice core scientist who may not be too familiar with it. Just 1-2 sentences would help them understand (even if of course, they could read the cited paper).

We added descriptions in the revised manuscript (section 3.1.2, line 242 – 245 in the revised manuscript with track changes).

Line 270 : precise before/after gravitational correction.

In the revised manuscript, we noted as "Note that all $\delta O_2/N_2$, $\delta Ar/N_2$, and $\delta^{18}O$ data in this and following sections are gravitationally corrected (see section 2.2)." at the first paragraph of the Result chapter.

Line 310 : You say that highly fractionated bubbles and clathrates are stratified in mm scale samples. Then, if you average over a certain depth, do you retrieve a better signal? Later on, you say 50cm, but here, you could go into a bit more detail, and justify this number. I also wonder if averaging is enough, or if, in addition to this layering, you have selective fractionation (perhaps post coring, or diffusion) that creates a bias.

The reviewer is right that if we average over a certain length, we should be able to retrieve a better signal. We agree that we can explain the idea and justify the acceptable length here.

The justification of the 50 cm is as follows. On the one hand, the acceptable scatter of $\delta O_2/N_2$ around the orbital-scale low-pass filtered curve is ~2 ‰ (one standard deviation), as seen for the depths just below the BCTZ (1200 – 1480 m) where the similarity to local summer insolation is observed. Also, the dataset of Kawamura et al. (2007) has scatters of 1.2 – 1.3 ‰ around the orbital-scale $\delta O_2/N_2$ variations. On the other hand, if we add a thin (e.g., 1-mm-thick) layer with extremely fractionated $\delta O_2/N_2$ of +1000 ‰ at one end of a 50-cm-long sample, it creates an anomaly of +2 ‰ (1000 ‰ × 0.1 cm / 50 cm) to the original $\delta O_2/N_2$ of the 50-cm sample. The exact thickness and $\delta O_2/N_2$ of anomalous layers can vary in real situations, but the above assumption is quite extreme (assuming all air inclusions in the thin layer has the maximum $\delta O_2/N_2$ observed by Raman spectroscopy), thus we expect that the length of 50 cm is sufficient for "diluting" the effect of anomalous layers.

The reviewer is also correct that the averaging would only work if we can eliminate the selective fractionations such as by post-coring gas loss. As we indeed excluded the gas-loss-fractionated outer ice from our dataset, we believe that the averaging is enough with our data. We emphasized in the revised manuscript that the removal of gas-loss fractionated outer ice is a prerequisite.

We added above discussion at the end of the second paragraph of section 4.2.

Line 325: lower dissociation pressure should produce a steeper Ar partial pressure of gradient from bubbles to clathrate. Why? Can you explain a bit more ? (it's maybe obvious to you, but not to me)

The description in the original manuscript was too brief and imprecise, thus we modified this sentence as line 411 – 419. The basic idea is that the gas flux from bubbles to clathrates depends on permeation coefficient and dissociation pressure (Salamatin et al., 2001), with higher permeation coefficient and lower dissociation pressure leading to larger flux. For the case of O_2 and Ar, the former has a *higher* permeation coefficient and *higher* dissociation pressure, thus their effects on the flux should cancel to each other.

Paragraph near line 355 : Add that nucleation increases dO2/N2. If you average over two annual cycles of Ca, do you get back a good value or is it also biased? Is there a selective loss for some layers?

We added that nucleation increases $\delta O_2/N_2$ and $\delta Ar/N_2$ as line 458 – 459.

It appears that the averaging over two cycles of Ca, which seems to roughly correspond to red lines (25-cm average) in Fig. 6, may be sufficient for obtaining a good value, with slight biases in some cases (1292 m in Fig. 6).

Could the correlation to Ca also be due to different bubble sizes for different densification rates in the firn, like in Freitag's papers?

We do not think that the correlation to Ca is related to the densification rate of firn. If Ca or some impurities (see below for a supplementary note) make smaller pores and enhance firn densification, the high-impurity layers close off earlier than the low-impurity layers in the close-off region in firn. This would promote bubble compression and thus O_2 depletion in the high-impurity layers. Thus, the correlation between Ca^{2+} and $\delta O_2/N_2$ from this mechanism is expected to be negative, which is opposite to the observation.

As a supplementary note, on the link between impurities and firn densification rate, Fujita et al. (2014, 2016) suggested that, based on the observations of firn at Dome Fuji in Antarctica and NEEM in Greenland, the actual active agent for the layered firn densification rates are ions such as Cl^-, F^- and NH_4^+, and the correlation with Ca^{2+} is possibly superficial (as Ca is a major element to form salts). In our high-resolution ion data, the correlation between the ions (Cl^-, F^- and NH_4^+) and Ca^{2+} are generally low because they are mobile in ice so that they are lost during firn densification or smoothed in ice. In any case, the layered firn densification rate is probably irrelevant to the observed correlation between Ca^{2+} and $\delta O_2/N_2$, as explained above.

Fujita, S. et al. (2014). Densification of layered firn of the ice sheet at NEEM, Greenland. *Journal of Glaciology*, *60*, 905–921. http://doi.org/10.3189/2014JoG14J006

Fujita, S et al. (2016). Densification of layered firn in the ice sheet at Dome Fuji, Antarctica. *Journal of Glaciology*, *62*(231), 103–123. http://doi.org/10.1017/jog.2016.16.

Line 368: Here, it's difficult to understand the hypothesis, the inputs and the results. What mechanisms are you taking into account? Do you start with very high bubble/clathrate layered concentrations?

We test whether the decreasing scatters below BCTZ are due to diffusive homogenization of layered displacement of gas molecules originally created in the BCTZ (thus not due to disturbance of insolation signal on the gas fractionation at the firn-ice transition in the past). We also test different permeabilities proposed by several studies. The only mechanism in the model is the molecular diffusion through the ice lattice driven by the concentration gradient of dissolved gas in the ice, which is in equilibrium with clathrate hydrates. The initial conditions of the model are the actual $\delta O_2/N_2$ and $\delta Ar/N_2$ profiles at 1258 m, which show highly layered values, and we let the model homogenize the layerings. The evolutions of temperature and thinning are incorporated in the model to mimic the real ice sheet condition (the depth profiles of thinning and temperature are assumed to be constant through time). We obtain the smoothed $\delta O_2/N_2$ and $\delta Ar/N_2$ profiles according to the elapsed time, and compare the model results with the high-resolution continuous ice-core data to assess the model results with different permeabilities. Please note that a similar simulation has been conducted by previous authors (Bereiter et al., 2014), but the study was limited without continuous high-resolution ice-core data to compare; thus, this is the first study that we can directly compare the model results with the detailed $\delta O_2/N_2$ and $\delta Ar/N_2$ in the ice sheet.

In the revised manuscript, we modified the descriptions about the model as the following: (1) Methods and Appendix now include the aim and setups of the model, and (2) the description at lines 368 – 376 of the original text were moved to Results, and (3) the following text was added to the fourth paragraph in the Discussion chapter.

"This study, for the first time, directly compares the diffusion model results with the detailed $\delta O_2/N_2$ and $\delta Ar/N_2$ in the ice sheet. The model could reproduce the smoothing of layered gas compositions as seen in the high-resolution continuous data (Fig. 10a and 11b). Also, the relationships between $\delta Ar/N_2$ and $\delta O_2/N_2$ in different zones (bubbles, BCTZ and clathrates) are similar to each other (slope of around 0.5). From these observations, we conclude that the large scatters just below the BCTZ originate in layered gas fractionations in the lower BCTZ, and that the subsequent decrease of scatters is due to diffusive homogenization. We thus disfavor the possibility that calls for a failure of the recording mechanism of insolation variations during the past firn-ice transition to generate the high scatters of $\delta O_2/N_2$ and $\delta Ar/N_2$ in and below the BCTZ.

Line 389 : explain where the 50cm nb comes from, maybe above.

See above.

Figure 7: add some vertical bars to help the reader.

We added vertical bars.

Figure 8 and 9 : it would be useful to put them on the same figure (except panel 1), to help the comparison.

Differences in axes ranges of bulk data and those of pair differences are too large to show in the same figure. Thus, we combined Figure 8 and Figure 9 in the same figure. The ratio of ranges of horizontal and vertical axes is 1:1 for each panel for easy comparisons of the slopes, except for panels (a) and (b).

Reply to Referee #2 (27 August 2021)

The article "Fractionation of O2/N2 and Ar/N2 in the Antarctic ice sheet during bubble formation and bubble-clathrate hydrate transition from precise gas measurements of the Dome Fuji ice core" by Ikumi Oyabu presents new δO2/N2 and δAr/N2 data, measured on Dome Fuji ice cores using the method of Oyabu et al. 2020. The authors are able to provide data from samples stored at low temperatures of -50°C in the freezer and show that under these conditions gas loss fractionation after coring is almost negligible. They also discuss their data in the context of a wide range of δO2/N2 and δAr/N2 measurements from other ice core sites and other measurement and storage strategies. They examine their data in four depth intervals attributed to different fractionation mechanisms (bubble ice, upper BCTZ, deep BCTZ and clathrate zone) through a simple regression analysis of δO2/N2 versus δAr/N2 and δO2/N2 versus δ18O-O2 to disentangle possible fractionation mechanisms (mass-independent/size-dependent vs. mass-dependent fractionation). Furthermore, the authors show that using a simple diffusion model to model permeation in conjunction with high-resolution data can explain the reduction in data variance due to diffusive smoothing in the clathrate hydrate zone.

The paper is well written and structured. I enjoyed reading this paper and look forward to its publication. Most of my "major" criticisms of this work have already been addressed by reviewer 1, and I am pleased to see how the authors have responded. In particular, the new schematic illustration about the different fractionation mechanisms will help the reader to understand the work better. There are only a few minor points to change, which I list below.

Minor points:

Line 15: Please avoid expressions like "high precision" or specify with numbers.
We removed “at high precision” (line 15 in the revised manuscript with track cahnages).

Line 21: Yes, analysing long ice samples can help to average the data scatter later, but how long should these samples be? Please specify a number here.
We added the proposed length (line 21).

Line 72/73: Please combine minus sign and number in the same line.
Yes, we will check the format in the proof.

Line 160ff: For the data shallower than 800 m, I do not see much agreement with the insolation data. The depth range is too short to support this statement. For the deeper depth range, I agree.

We agree that the age range for the data shallower than 800 m is too short to robustly compare with the insolation curve as we could for the deeper part. However, for the shallower depths, we think we can identify the similarity of $\delta O_2/N_2$ and insolation curve in that both curves show two peaks at ~350 m (12 kyr) and ~700 m (32 kyr), and that the second peak (~700 m) is larger than the first one. The comparison of $\delta Ar/N_2$ with the insolation curve is even less robust perhaps because the signal-to-noise ratio of $\delta Ar/N_2$ is smaller than $\delta O_2/N_2$. We have also observed that $\delta Ar/N_2$ has sometimes slightly different phasing with respect to $\delta O_2/N_2$ (in our ongoing measurements for older ages).

We modified the text as line 199 – 215.

Line 161: "We evaluate ... low-pass filtered curves": Please indicate here the cut-off period used and explain how the low-pass filtering was performed.

The filter is the same filter as used by Kawamura et al. (2007). Explanation was added (line 216 – 218).

Line 255/256: As already stated, the similarity of the bubble-ice data to the solar radiation curve is not robust in my opinion.

We agree that the similarity is less robust than for the deeper depths, which may be mostly due to the (inevitable) short length for comparison as discussed above, thus we weakened the statement and describe this part as a simple observation and consistency with the proposed mechanism (occurring in association with the bubble formation processes) (line 324 – 325).